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Multiple Quantum and Dipolar Correlation Effect NMR Studies of Cross-linking in Elastomer Systems

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Introduction

Physical and chemical aging of filled polydimethylsiloxane-polydimphylsiloxane (PDMS-PDPS) copolymer foams is currently being studied to assess engineering performance degradation and to provide fundamental understanding of aging mechanisms for predictive modeling. Nuclear Magnetic Resonance (NMR) spectroscopy has been shown to be a powerful method for the characterization of polymer aging mechanisms. NMR offers the ability to assess speciation changes and changes in motional properties caused by chemical and physical aging mechanisms. In fact, the measurement of ^1H transverse relaxation times (T_2) of aged silica filled PDMS/PDPS copolymers have been shown to be sensitive to bulk changes in motional processes caused by aging mechanisms such as radiation exposure [1-3]. However, more subtle aging mechanisms cause only small changes in bulk relaxation times and conclusive interpretation of the NMR data can be difficult. ^1H T_2 studies of surveillance return samples, for example, have suffered from such an insensitivity to age and no direct correlation between age and relaxation time have been detected, mirroring solvent swelling results.

Figure 1. Spin-echo decay curves for surveillance return samples.
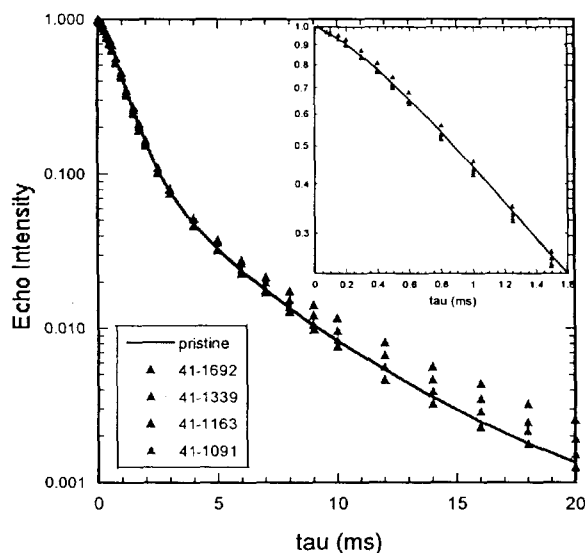
Close examination of the echo decay functions for surveillance return elastomers sample shows that the main difference between samples are (a) the degree of non-exponential decay behavior at early times between samples (see inset, figure 1), and (b) the amount of material that can be characterized by a long T_2. Local and long range structure have important implications on the motional properties of the polymer chains. In PDMS based polymers the couplings between protons within methyl groups are attenuated by rapid spinning about the C_3 axis and by the more complex translational and rotational motion of the polymer chains. Crosslinks and entanglements reduce the amplitude and frequency of such long-range segmental motions. The result is that dipolar couplings between protons are not completely averaged to zero. The non-exponential decay is a direct consequence of the remaining, residual dipolar couplings [4].

A recent series of papers [4-11] has detailed experimental strategies for quantitative analysis of residual dipolar couplings and has demonstrated correlations of residual dipolar couplings with

cross-link density. Further, it has been shown for a number of model systems that the residual dipolar coupling can selectively measure changes in bulk crosslink density without interference from the presence of a filler phase [11]. In light of this we have applied these new methods to selectively measure residual dipolar couplings to determine aging in the silica filled PDMS based foams. We have applied a 2 dimensional double quantum (DQ) correlation NMR [7,12,13] and a modified echo approach [6,8] to quantify the residual dipolar coupling in the polymer foams. We have first tested these methods on γ-irradiated foams that have been extensively characterized by solvent swelling and T_2 NMR analysis [1].

Experimental

The materials tested were a copolymer of polydimethylsiloxane and polydiphenylsiloxane, crosslinked by a vinyl monomer/vinyl-specific catalyst system. The percentages of each monomer unit in the base rubber were 90.7% PDMS, 9.0% PDPS, and 0.31% polymethylvinylsiloxane. This rubber was then milled with a mixture of fumed and precipitated filler (21.6 and 4.0 wt%, respectively), and 6.8 wt% of an ethoxy end-blocked siloxane added as a processing aid. The composite was studied in foamed form made by processing the filled polymer with prilled urea, which is subsequently washed out. M9750 and M9760 are the designations for the porous filled polymer foams, exhibiting 50 and 60 percent porosity respectively. Samples were irradiated in a stainless steel container (V ~ 2 liters) that was exposed to a Co^{60} source (0.5Mrad/hr) for various periods of time. Vacuum samples were encapsulated in glass tubes (20 minutes pump time, 1 mtorr), while air irradiated samples were left open to the air environment inside the container. All experiments were performed at the same dose rate.

The following surveillance return samples were also studied: S255546 s/n's 1163, 1692, 1358, 1197, S255541 s/n's 1339, 1091, 1237, 1626, S545505 s/n's 2041, S545506 s/n's 2081, 1893, 1181, and S545507 s/n's 2834, -2679, 1286.

^1H T_2 *measurements* and ^1H *DQ 2D NMR measurements* were performed at 500.13MHz on a Bruker DRX-500 spectrometer using a HCX 5mm probe. ^1H Excitation pulses of 7µs and relaxation delays of 10 seconds were used. In all cases, small (0.5cm x 0.5cm) squares of foam were cut from the larger foam and set in the portion of a 5mm NMR tube that would be within the coil volume of the probe. T_2's were determined by fitting the decay of Hahn spin-echo intensity with echo delay time as detailed previously, to a double exponential decay. Errors in T_2 values were estimated from analysis of 4 replicate runs for 3 different samples. For the replicate runs, separate samples of the foams were cut from the samples provided. DQ experiments were performed with a standard 90-t-180-t-90-t_1-90-acquire (t_2) pulse sequence (8,13,14). The 2D time domain data set was processed in magnitude mode in t_2. DQ intensities were scaled for differences in sample mass and fits to the intensity versus DQ preparation time were performed by a non-linear least squares fit of the data. Q_{DC} *experiments* were performed by measuring the intensity of the stimulated echo for delays t_1 and t_2 (7,9) and the intensity of the primary echo for delay t_1. The ratio of the stimulated to the primary echo (A_{stim}/A_{prime}) is defined as the dipolar correlation coefficient (Q_{DC}). Experiments were performed at 299.995MHz in a field gradient of 2G/mm. Measurements of spin-echo intensity as a function of field gradient showed that this gradient strength was below the gradient where decay due to diffusion would occur. 90° pulse widths of 3.7µs were used with t_2=50ms. For the stimulated echo, a long decaying component due to free polymer chains was subtracted from the data before dividing by the intensity of the prime echo.

Results

Figure 2 shows the 2D double quantum (DQ) filtered spectrum of pristine foam. The DQ sequence serves to filter out responses due to uncoupled spins [12] and DQ-filtered spectra take the form of a correlation map where signal intensity is due to the presence of residual dipolar couplings, $<\Omega_{dred}^2>$, between spins. Further, it has been shown [11] that the initial rate of change of the DQ signal with preparation time is proportional to $<\Omega_{dred}^2>$. DQ growth curves for the M9760 foam irradiated to cumulative doses of 0, 5, and 50Mrad gamma radiation measured a linear relationship between the residual dipolar coupling between methyl spins and increased exposure, suggesting an increase in cross-link density.

We have also applied a recently reported method developed by Kimmich and coworkers to determine time fluctuations in the residual dipolar coupling. This method relies on measuring the ratio of a solid echo to a stimulated echo and has been termed dipolar correlation NMR. In brief, the ratio of the stimulated echo to the solid echo, termed the Dipolar Correlation Quotient (Q_{DC}), effectively filters out the fast motional processes and Q_{DC} thus decays only according to fluctuations of the residual dipolar coupling in the kHz range, $<\delta\Omega_d^2>$ [6,8]. For exponential correlation functions, this relationship can be described as:

Figure 2. DQ filtered spectrum of pristine M9760 foam with a DQ preparation time of 1ms.
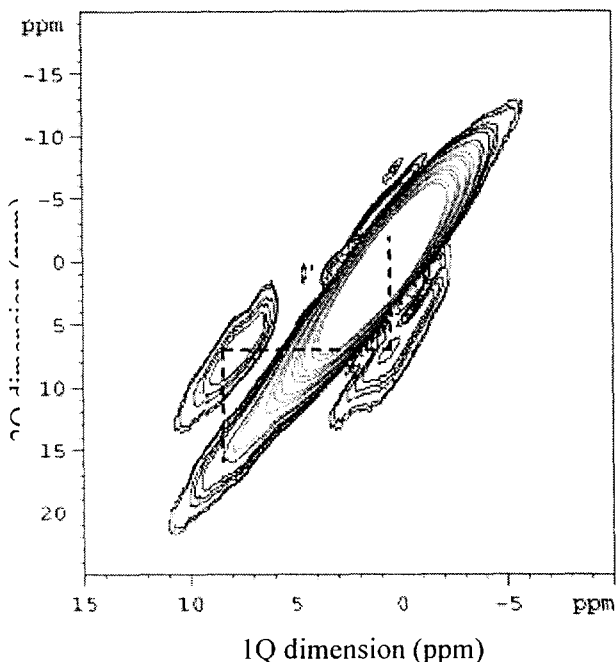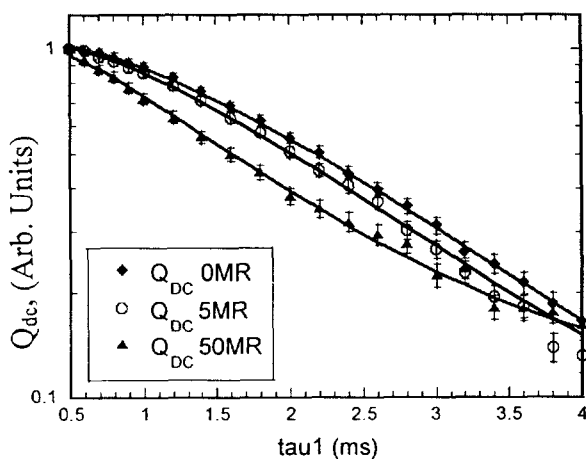

1Q dimension (ppm)

Figure 3. Decay of Dipolar Correlation Quotient, Q_{DC}, for M9760 foams as a function of cumulative dose.

$$Q_{DC} = \exp(-0.25 <\delta\Omega_d^2> C_1)$$

The Q_{DC} decay functions for the γ-irradiated samples are shown in Figure 3 and show that $<\delta\Omega_d^2>$ increased with increased exposure.

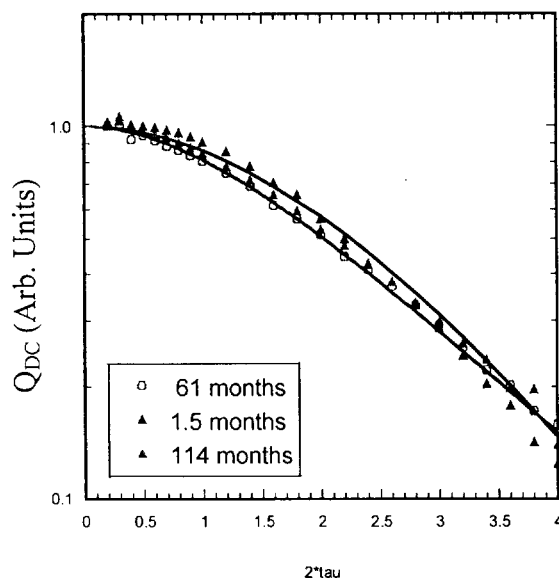The Q_{DC} results mirror quite well the DQ results, showing that $<\Omega_d>$ and $<\delta\Omega_d^2>$ increased with cumulative dose. This observation is further evidence that the number of topological constraints, and thus the cross-link density, increased with increased radiation exposure.

It is interesting to note that T_2 measurements alone have suggested that a significant amount of structural relaxation occurs at low cumulative dose due to a change in the polymer filler interaction [1]. While both DQ and Q_{DC} experiments show a difference between filled and unfilled foams, the $<\delta\Omega_d^2>$ and $<\Omega_{dred}^2>$ measured here seem insensitive to changes in the interfacial bonding caused by irradiation and appear to have measured only changes in bulk polymer dynamics. The insensitivity of these methods to changes in filler contribution has been observed previously in carbon black filled polybutadiene [13]. There are two likely possibilities for this insensitivity. The interaction with the filler serves to bind large domains of the polymer chain while leaving other large portions free. In both the DQ method and the Q_{DC} method, certain pulse sequence delays at the beginning of the data acquisition period serve to filter out spectroscopic signals from slow motion domains at the interface. Slower motion domains

would be expected to decay rapidly, perhaps decaying within the time frame of the acquisition delays (50μs in the DQ and 0.5ms in the Q_{DC} experiments). Spin-echo experiments do not suffer as strongly from this limitation and thus effects due to both rapid and slow motional domains will influence the decay rate. If irradiation initially causes a partial rupture in the interfacial bonding, an increase in the amount of free polymer would occur. The motional properties of the released polymer would then be described by the topological constraint density characteristic of the free polymer while the polymer domains remaining on the surface would still be unobservable.

We have applied the Q_{DC} method to the analysis of surveillance return (SR) samples in the S5455 series (similar in composition to the M97 materials) and the Q_{DC} decay curves for three samples are shown in Figure 4. As can be seen, the decay curves are remarkably similar and can be characterized by $< \delta \, \Omega_{dred}^2 > = 1.0\pm0.2 \, x10^6 \, s^{-2}$. Fits to the data indicate that the difference in $< \delta \, \Omega_{dred}^2 >$ between the samples with a service lives of 1.5 and 114 months is less than 20% but within experimental error. This suggests that the relative amounts of topological constraints are remaining fairly constant with age. Further experiments are ongoing to confirm these findings.

Figure 4. Q_{DC} as a function of τ_1 for $\tau_2 = 50$ms for S5455 foams as a function of age.

Conclusions

The above report details the ^{1}H NMR analysis we have performed to characterize the aging signatures that may exist in silica filled PDMS/PDPS based copolymer systems. We have performed numerous ^{1}H NMR experiments on pristine, γ-irradiated, and SR samples to assess the ability of these experiments to characterize aging mechanisms. Previous T_2 measurements have shown that a significant amount of structural relaxation occurs at low cumulative dose due to a change in the polymer filler interaction in γ-irradiated samples while SR samples show little correlation with age. However, measurements of residual dipolar couplings in both γ-irradiated and SR samples have shown changes in cross-link density that correlate reasonably with age. Variable temperature spin-echo experiments have also been able to characterize changes in entanglement density due to aging mechanisms in SR samples.

Values of $< \delta \, \Omega_{dred}^2 >_{Me-Me}$ measured by DQ and Q_{DC} NMR methods seem to be insensitive to changes in the interfacial bonding, measuring only changes in bulk polymer dynamics. T_2 measurements show sensitivity to both cross-link density and interfacial changes. In view of these observations, it should be possible to design a NMR spectroscopic approach to quantitatively characterize changes in crosslink density and interfacial interactions by rapid ^{1}H NMR analysis.

Acknowledgements

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